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In re Patent application of:)
Hisato SHINOHARA et al.)
Serial No. 08/169,127) Group Art Unit: 1506
Filed: December 20, 1993)
For: METHOD AND SYSTEM OF)
LASER PROCESSING)

VERIFICATION OF TRANSLATION

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Washington, D.C. 20231

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that I am well acquainted with both the Japanese and English Languages;

that I am the translator of the attached translation of Japanese Patent Application No. 61-229252 filed on September 26, 1986; and

that to the best of my knowledge and belief the following is a true and correct translation of Japanese Patent Application No. 61-229252 filed on September 26, 1986.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed

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Dated this 6th day of March, 1995



Kunitaka YAMAMOTO

PATENT APPLICATION

September 26, 1986

Commissioner of Patent Office:

1. Title of the Invention

Photo Processing Method

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4. List of Attachments

(1) Specification One copy

(2) Drawings One copy

(3) Copy of Application One copy

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SPECIFICATION

1. TITLE OF THE INVENTION

PHOTO PROCESSING METHOD

2. CLAIMS

- 5 1. A photo processing method comprising the steps of expanding a pulsed laser beam having a wavelength 400 nm or less into a rectangular shape having a large area by means of an optical system, restricting said laser beam in a direction along the shorter side of said rectangular shape; condensing the restricted laser beam through a cylindrical lens in order to further narrow the width of the beam, and irradiating a surface with the condensed laser beam in order to form a groove.
- 10 2. The photo processing method of claim 1 wherein said thin film to be processed is a transparent conductive film.

15 3. The photo processing method of claim 1 wherein said pulsed laser beam is of an excimer laser light having a pulse width of 50 n sec or less.

3. DETAILED DESCRIPTION OF THE INVENTION

[Field of the Invention]

20 The present invention relates to a selective processing method for patterning a thin film of solar cells or display devices or the like, in which instead of using a photoresist, the thin film is directly scribed with a line-shaped U.V. light.

[Prior Art]

A laser process using a YAG laser (having a wavelength 1.06 μm) is known for processing a transparent conductive film without using a photoresist.

5 In the laser process using this wavelength, a spot-like beam is radiated on an object to be processed and is scanned in one direction so that a groove is formed into a chain-like shape, which is a series of spots. Because of this, the scanning speed of this beam and an energy density necessary for the processing have a very sensitive mutual effect
10 one another as well the thermal conductivity and the volatility of the processed material. Therefore, it has a drawback that a margin for ensuring an optimum quality with an improved industrial productivity is small. Further, the optical energy of the above laser light has only
15 1.23 eV (1.06 μm). An optical energy band gap of a glass substrate or an object to be processed which is formed on a semiconductor, for example, transparent conductive film (CTF hereinafter) is 3 - 4 eV. Therefore, tin oxide, indium oxide (including ITO), zinc oxide or the like do not have a sufficient light absorption property with respect to a YAG
20 laser. In the case of using a Q switch oscillation in a YAG laser, the laser process must be performed with an average beam intensity as high as 0.5 - 1 W (in the case of a beam diameter being 50 μm , focus length 40 mm, pulse frequency 3 kHz, pulse width 60 n sec) and with a scanning speed in the range of 30 - 60 cm/minute. As a result, although it is possible to process a CTF with this laser, the substrate thereunder such
25 as a glass substrate is damaged and a micro crack occurs therein.

[The Problems To Be Solved By The Invention]

In the process using the YAG laser, because scanning is done by repeating the emission of a spot-shaped beam, micro cracks caused to an underlying substrate have a shape which is similar to an outer periphery of the laser beam, that is, a "scale"-like shape.

5 Also, in the method using a Q switch oscillation in a YAG laser, the peak output of the laser beam tends to vary during the long use thereof so that it is necessary to monitor the output at each time.

Further, it was entirely impossible to selectively form a number of fine patterns having a width of 10 - 50 μm on a same plane. Also, since
10 the CTF material of the irradiated portion is not sufficiently changed to be insulative, it was necessary to perform etching with acid solution (hydrofluoric solution or the like) in order to completely change it to be insulative.

The present invention is directed to an improvement of Japanese
15 Patent application No. 59-211769, filed on October 8, 1984 by the applicant of the present invention.

[Means To Solve The Invention]

The present invention is to solve the foregoing problems, and specifically, one or plural pulses of a pulsed laser having a wavelength not longer than 400 nm (i.e. 3.1 eV or higher in terms of energy)
20 irradiated for conducting a line-shaped patterning, which is not a beam
 spot of 20 - 50 $\mu\phi$ but is a line-shaped beam having a width of 20 - 200
 μm (for example, 150 μm) and a length of 10 - 60 cm, for example, 30
 cm. In this manner, by irradiating with a line shaped pulsed laser
25 having a wavelength of 400 nm or less (pulse width 50 n seconds or less), the light absorption efficiency by a CTF is increased to 100 times

as high as in the case of using a YAG laser ($1.06 \mu\text{m}$), resulting in that a process speed is increased to 10 times or more.

Further, rather than using the YAG laser of which initial light has a circular shape and has an Gaussian distribution in intensity, an excimer 5 laser is used in the present invention. Therefore, the irradiation surface of the initial light has a square shape and the intensity is approximately uniform throughout the irradiation surface. Therefore, the width of the initial light is expanded by means of a beam expander in order to form a rectangular beam having a large area. After that, the laser light is 10 condensed to be a slit shape in either one of X or Y direction by means of a rod like lens, i.e. a cylindrical lens. However, when the width of the condensed light is made $50 \mu\text{m}$ or less, the spherical aberration of the cylindrical lens (rod like condensing lens) can not be neglected. Accordingly, a region in which the intensity is lower in accordance with 15 a Gaussian curve will occur at the periphery of the condensed light. As a result, the periphery of the line becomes unclear. Moreover, it becomes further impossible to form grooves in the shape of a line having a width of $10 - 30 \mu\text{m}$, for example, $20 \mu\text{m}$. For this reason, in the present invention, a laser beam is passed through a slit before entering a 20 cylindrical lens in order to be restricted into such a width so that the spherical aberration of the cylindrical lens can be neglected, and then the beam is condensed by the cylindrical lens to a width of $10 - 30 \mu\text{m}$ having a clear edge.

As a result, it is possible to form a very thin groove pattern of 20 25 $\mu\text{m} \times 30 \text{ cm}$ which has clear peripheral edges without the influence of a spherical aberration. Also, the width of a portion of the pattern may be

broadened up to 100 μm .

[Function]

The emission of one or plural pulses onto one place through the slit makes it possible to form a line shaped groove having a length of 10-60 cm, for example, 30 cm, and having a width of 10 - 30 μm which is very thin without being influenced by the spherical aberration. Also, since a pulsed laser light is used instead of a YAG laser of a Q-switch method, the peak output power can be precisely controlled.

As a result, it becomes possible to selectively remove an object to be processed, for example, CTF to pattern a slit-shaped groove thereon, and at the same time, by introducing a vacuum, clean air or nitrogen into a space between a mask and the object to be processed, the product of the object formed by the laser irradiation can be directed downwardly.

Also, the residues remaining after the formation of the groove on the object can be removed by an ultrasonic cleaning with a cleaning liquid such as alcohol or acetone. Therefore, many steps such as a so called resist coating, an etching of the object, or removal of a photoresist, becomes unnecessary as well as the use of a polluting material.

In addition, since the slit is installed in the optical system before condensing the laser beam, there is substantially no damage to the slit by the laser light. Also, the accuracy of the mechanical processing with respect to the gap of the slit is not so strict and the shape of the laser beam is determined by being condensed by the cylindrical lens.

[Example 1]

Fig. 1 shows a laser processing system using an excimer laser. An excimer laser (1) (wavelength 248 nm, $E_g = 5.0$ eV) is used. This laser has an initial beam of 16 mm x 20 mm as shown in Fig. 2(A) and has an energy of 350 mJ since the efficiency is 3 %. This laser beam is expanded to a large area by a beam expander (2). That is, it is expanded to be 16 mm x 300 mm as shown in Fig. 2, (21). The energy density is 5.6×10^{-2} mJ/mm² at this stage.

Next, the laser beam is passed through a slit (3) having a gap of 2 mm x 300 mm in order to obtain a laser beam (13) of 2 mm x 300 mm as shown in Fig. 2(C).

Further, the laser beam is condensed through a cylindrical lens (7) comprising synthetic quartz so that the width of a groove on a processing surface becomes 20 μm . (Fig. 2(D)) Although the slit may be of any width, it is necessary to restrict the laser beam to such a degree that the spherical aberration of the cylindrical lens does not influence. Also, the width of the groove on the object can be arbitrarily selected depending upon the performance of the cylindrical lens.

As shown in Fig. 3, a slit-shaped beam (23) with a length of 30 cm and a width of 20 μm was directed onto an object (11) on a substrate (10) so that a groove (5) was formed.

In the case of the present example, the surface to be processed was a substrate (10) having a transparent conductive film ($E_g=3.5$ eV) on a glass and the laser was an excimer laser (produced by Questec Inc.).

The light of 248 nm of a KrF excimer laser was used as a pulsed light. This is because the optical band gap of this light is 5.0 eV so that the object can absorb the light sufficiently and only the transparent conductive film can be selectively processed.

The irradiation was carried out with a pulse width of 20 n sec. and with a repetition frequency of 1 - 100 Hz, for example, 10 Hz. Also, tin oxide (SnO_2) which is conductive transparent film (CTF) formed on a glass substrate was treated.

When the film was processed, the irradiation with only one pulse of the line-shaped laser beam made a groove (five CTF) completely opaque and into fine powder. This was subjected to ultrasonic cleaning (frequency 29 kHz) with an acetone aqueous solution for 1 - 10 minutes so that the CTF was removed. The underlying sodalime glass substrate
10 was not damaged at all.

Fig. 2 is for explaining the condition of the laser beam shown in Fig. 1. That is, the laser beam as emitted has a square shape (20) as shown in Fig. 2(A). This is expanded (21) in a lengthy direction by an expander as shown in Fig. 2(B). Further, short edges of the laser beam is
15 restricted (22) by the slit. Then, the short edges are further condensed by the cylindrical lens in order to form a beam (23) as shown in Fig. 2(D).

Fig. 5 shows that a plurality of grooves (15, 16, 17 ... n) are formed by irradiating with slit-shaped pulsed laser light onto the
20 substrate. In this manner, one groove is formed by the irradiation of one pulse. After that, a Y-table (Fig. 3, (10)) is moved to 15 mm and a next pulse is emitted so that a groove (16) is formed. Further, the table is moved to 15 mm and a next pulse is emitted to form a groove (17). In this manner, by emitting n pulses, a plurality of grooves were formed
25 on a large area and an (n+1) division was achieved.

Fig. 3 shows that a plurality of grooves (5, 6, 7, ... n) are formed by irradiating with slit-shaped pulsed laser light onto the substrate. In this

manner, one groove is formed by the irradiation of one pulse. After that, a Y-table (Fig. 3, (10)) is moved to 15 mm and a next pulse is emitted. Then, the table is moved to 15 mm and a next pulse is emitted. Thus, by emitting n pulses, a plurality of grooves were formed on a large
5 area by dividing into n parts.

[Example 2]

An amorphous semiconductor (mainly comprising silicon) which is added with hydrogen or fluorine is provided with an ITO (which is an indium oxide added with tin oxide at 5 weight %) with a thickness of
10 1000 Å by an electron beam evaporation as a surface to be processed.

With this surface face downward, it was irradiated with a pulsed light having a wavelength not longer than 400 nm in a vacuum (10^{-5} torr or lower) in accordance with the present invention. The wavelength was 248 nm (KrF). The pulse width was 10 n seconds. The average
15 output was 2.3 mJ/mm². Thereby, the ITO of the processed surface was volatilized and ITOs could be insulated by a formed groove without damaging the underlying semiconductor.

The other descriptions are the same as in Example 1.

[Effect]

In accordance with the present invention, when a plurality of grooves, for example, having a width of 20 µm and with an interval of 15 mm are formed at 10 Hz/pulse, a duration of 0.8 minute was sufficient. As a result, the number of steps could be reduced from 7 steps to 2 steps (irradiation, cleaning) as compared with the conventional method in which a photoresist is sued in a mask-alignment manner, and also the process time could be reduced to 5 - 10 minutes,
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hence, a number of line-shaped grooves could be obtained with a lower cost and a high productivity.

That is, in the present invention, since the slit is placed well apart from the surface to be processed and there is no photoresist used in contact with the surface, the life time of the slit is long. Also, it is not necessary to conduct steps such as photoresist coating, prebaking, light exposure, etching, and removal.

It was described in the present invention that the distance between grooves (i.e. the area to remain without processed) is larger, however, contrary to this, by connecting light irradiation one by one, the remaining area can be 20 μm while the removed portion is 400 μm .

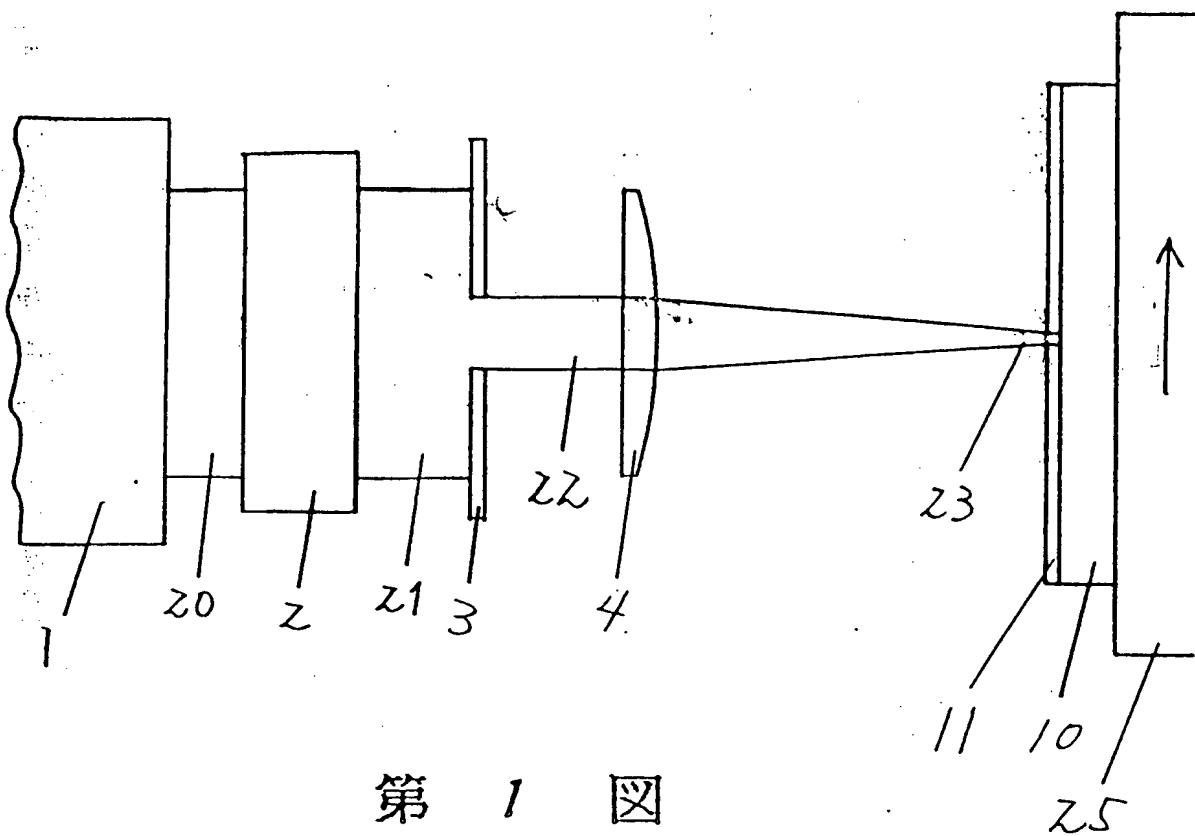
Further, in the optical system of the present invention, it is possible to insert an integrator, condenser lens and a projection lens in parallel between the beam expander and a surface to be processed in order to increase the accuracy of the system.

4. Brief Description of the Drawings

Fig. 1 shows a scheme of a laser processing method in accordance with the present invention.

Fig. 2 shows a variation in the pattern of the light.

Fig. 3 shows a manufacturing process of grooves on a substrate.



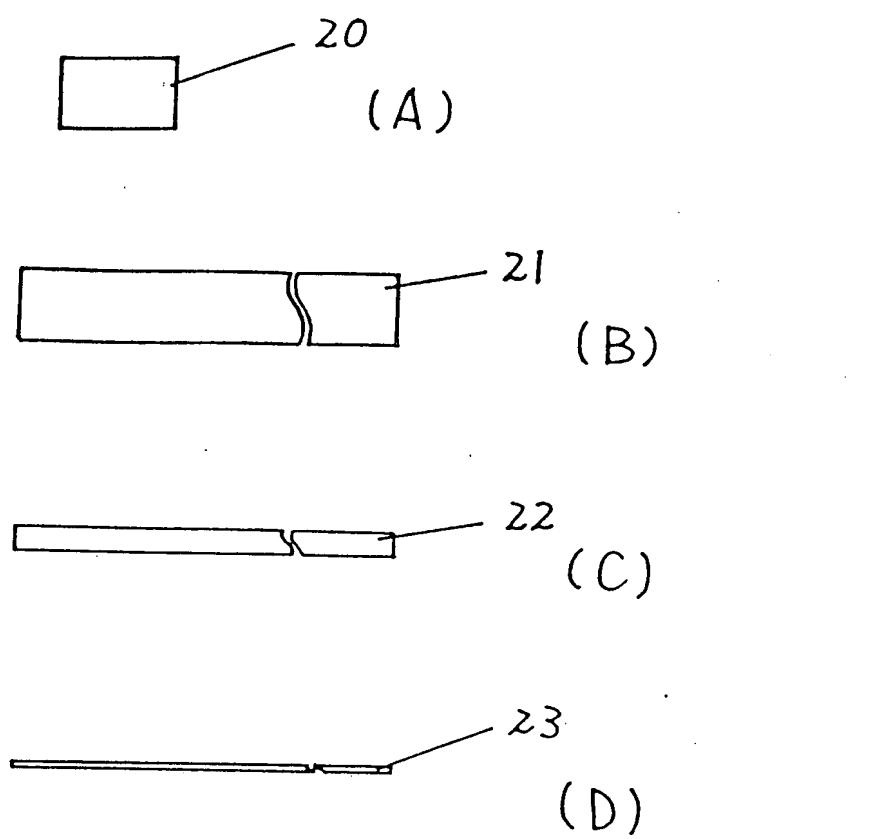
第 1 図

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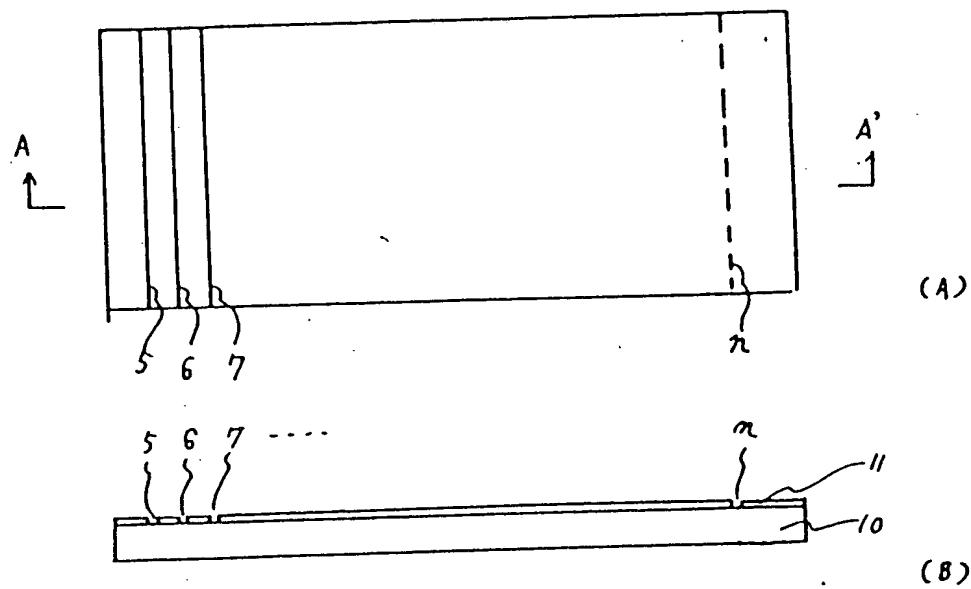




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